Structural distortions and orbital ordering in $LaTiO_3$ and $YTiO_3$

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Abstract. – Theoretical investigations of the electronic, magnetic and structural properties of $LaTiO_3$ and $YTiO_3$ have been made. In the framework of GGA and GGA+U scheme we analyzed the effect of the local Coulomb interaction (U) value on the atomic forces acting in the experimental structure. The optimal parameters of the electron-electron on-site interactions as well as the orbital configurations and magnetic properties are determined.

Introduction. – Transition-metal perovskite oxides $LaTiO_3$ and $YTiO_3$ are classical Mott-Hubbard insulators. In spite of the fact that they are formally isoelectronic with one $3d$ electron in the t_{2g} shell $LaTiO_3$ has a G-type antiferromagnetic (AFM) structure whereas $YTiO_3$ has a ferromagnetic (FM) one. The most unusual feature of these compounds relates with a nearly isotropic magnon spectrum in both titanates despite of their distorted crystal structures [1, 2].

There are two theoretical models aimed to explain these effects in $LaTiO_3$. One of them originates from the work of Kugel and Khomskii [3] and operates in terms of the lattice distortions and an orbital ordering (OO). Another one is proposed by Khalliulin and Maekawa [4] and describes the above effects by the model of orbital liquid (OL) where the fluctuations of orbital degrees of freedom play an important role. According to [4] the energy of the orbital fluctuations is estimated to be $W_{\rm orb} \sim 160$ meV. Thus OL model is applicable only if the splitting of the t_{2g} orbital in the crystal field Δ is significantly smaller than $W_{\rm orb}$. Otherwise the nearly isotropic exchange is likely to be due to an orbital ordering with a peculiar orbital configuration [9].

The OL model was supported by neutron experiments of Keimer *et al* [1] where no OO in $LaTiO_3$ was found. Fritsch with co-workers [5] made heat capacity and magnetic measurements. Having supposed the nearly cubic structure of $LaTiO_3$ they concluded that the energy of the spin-orbit coupling for Ti-sites was $E_{\rm SO} = 30$ meV and the crystal field effect was small. The theoretical estimations made by Solovyev in Ref. [6] in the framework of the local spin density approximation (LSDA) and LSDA+U theory showed that Δ in $LaTiO_3$ was as small

as 49 meV and this value was of the same order of magnitude as the energy of the spin-orbit (SO) coupling $E_{\rm SO} = 23$ meV.

Recent X-ray studies [7, 8] revealed a sizable deformation of the TiO_6 octahedra and deviation from the cubic symmetry in $LaTiO_3$ below $T_{\rm N}$. The splitting of the t_{2g}- levels due to crystal deformations was estimated in [7] to be about 240 meV, and 120-300 meV in [9]. This was also supported in the *ab-initio* calculations [10] in the framework of LDA and LDA+DMFT theory, where Δ was reported to be ~ 200 meV. Those values of Δ were larger than $W_{\rm orb}$ and could provide ordering of the t_{2g} orbitals. The OO-model has had a support in the *ab-initio* theoretical studies [10–13] for both $YTiO_3$ and $LaTiO_3$ as well as in the direct observations of the orbital ordering in $YTiO_3$ [14–16], and in $LaTiO_3$ [16] from the NMR spectra analysis.

The physical properties of both $LaTiO_3$ and $YTiO_3$ are strongly sensitive to the chemical composition [17]. The highest value of the Néel temperature in $LaTiO_3$ was reported by Cwik *et al* [7] and Hemberger with co-authors [8] to be $T_{\rm N} = 146$ K, while the magnetic moment was $\mu = 0.57\mu_{\rm B}$ [7]. This magnetic moment disagreed with the theoretical estimations of more than $0.8\mu_{\rm B}$ [6, 18]. For $YTiO_3$ the Curie temperature amounts to 30 K and $\mu = 0.84\mu_{\rm B}$ [15, 16, 19].

According to the OO model the difference in the magnetic properties of $LaTiO_3$ and $YTiO_3$ can be attributed to the different types of distortions (see for example Refs. [6, 7, 13]). The main distortion in $YTiO_3$ has the Jahn-Teller type, while the $GdFeO_3$-type distortion dominates in $LaTiO_3$. In this letter we investigate the nature of those crystal distortions and the effects of OO on electronic and magnetic properties of the $LaTiO_3$ and $YTiO_3$ taking the effects of local Coulomb correlations into account.

Methods and models. – Both $LaTiO_3$ and $YTiO_3$ have a P*bnm* crystal structure. The lattice constants and atomic positions are taken from [7, 19]. The structural parameters for $LaTiO_3$ used in the calculations correspond to the temperature below $T_{\rm N}$ ($T = 8$ K). The examination of the $YTiO_3$ is made for the high temperature structure ($T = 293$ K) only because there is no structural data for $YTiO_3$ at $T < T_{\rm C}$. The crystal structure relaxations are not performed but the calculated forces on atoms for the experimental atomic positions are used for the verification of the agreement between theory and experiment. The orthorhombic unit cell used in our calculations consists of four formula units. This cell allows us to consider both FM and AFM structures with different types of the magnetic ordering.

For electronic structure calculations we use the projected augmented wave (PAW) method [20, 21] in the framework of the density functional theory (DFT). The exchange-correlation correction is taken into account within the general gradient approximation (GGA) [22]. In order to treat the effect of local Coulomb interactions in a partially filled $3d$ band of Ti the LDA+U method is applied [23, 24]. The Brillouin zone (BZ) is sampled with the $7 \times 7 \times 5$ mesh with its origin at Γ point. The valence states include $2s$, $2p$ for O, $4p$, $4d$, $5s$ for Y, $3p$, $3d$, $4s$ for Ti and $5p$, $5d$, $6s$ for the La-atoms. The cutoff energy of the plane-wave expansion is 400 eV.

Results and discussions. – The results of our GGA calculations for $LaTiO_3$ and $YTiO_3$ are presented in fig. 1. We have found the non-magnetic ground state for $LaTiO_3$ and ferromagnetic ground state for $YTiO_3$ with the value of the magnetic moment $0.8\mu_{\rm B}$ per Ti atom. This magnitude of the magnetic moment is very close to the experimental value of $0.85\mu_{\rm B}$ [15, 16, 19].

In the right part of fig. 1 the total density of states (DOS) for ferromagnetic $YTiO_3$ calculated within GGA approach is shown by red color. It consists of three well separated sets of bands. The lowest in energy band lies from -8 till -4 eV and is predominantly of O-$2p$ character. The t_{2g} states of Ti are strongly polarized. Spin up crosses the Fermi level whereas the spin down is completely empty and lies above the Fermi energy, thus $YTiO_3$ is a half

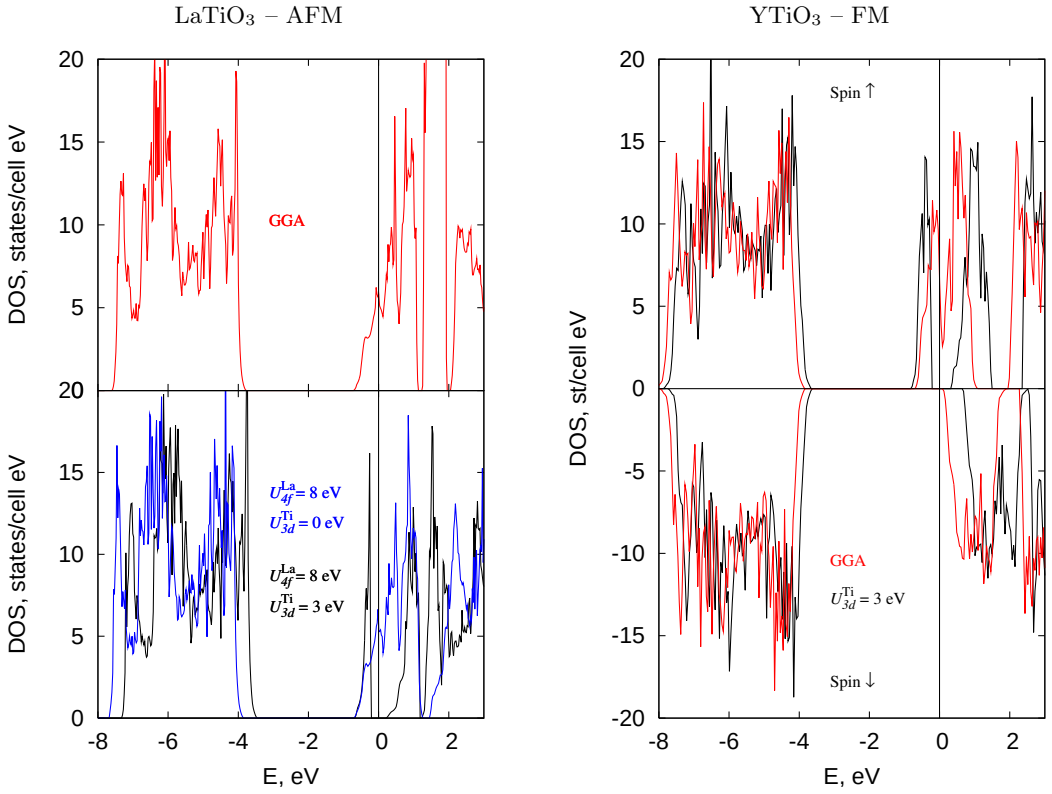

Fig. 1 – (*color online*) DOS of the AMF (G-type) $LaTiO_3$ (*left*) and FM $YTiO_3$ (*right*) in the framework of the GGA (*red*) and GGA+U (*blue* and *black*, see text) respectively. Upper and lower panels in $YTiO_3$ are up and down spin states.

magnetic ferromagnet in our GGA calculations. The bandwidth of the t_{2g} states is about 1.8 eV for both spin channels. The e_g states of Ti and the rest unoccupied states (O3s, Ti4p, etc.) are higher in energy and separated from t_{2g} states by a small gap. Our results are in good agreement with the early study of this compound [12, 25].

In the upper left part of fig. 1 the total DOS for $LaTiO_3$ is shown. In this case the DOS is non-spin-polarized and consists of four parts. As in $YTiO_3$ the fully occupied band of O-2p character is located from -7.8 to -4 eV. The t_{2g} states cross the Fermi level and have the bandwidth about 1.9 eV. The e_g states lie starting from 2 eV. In the energy region between t_{2g} and e_g states the La-4f band is located. This band ordering Ti-t_{2g}, La-4f, Ti-e_g is not compatible with the results of early calculations [6, 10, 11, 18, 26] and with the experimental data [27]. The simplest way to fix this problem is to apply GGA+U approach for the La-4f states. The results of the calculation of $LaTiO_3$ with a value of Coulomb repulsion $U_{4f}^{\mathrm{La}} = 8$ eV are shown on the left down part of fig. 1 by blue color. The value of Coulomb interaction used is in good agreement with the experimental and theoretical estimations [11, 18, 28]. The obtained band ordering is now in consistency with the previous studies [10]. In the rest part of the paper we will always use this result as a starting point for the following considerations without explicit mentioning and will refer to this calculation as GGA.

According to experiments [27, 28] both $LaTiO_3$ and $YTiO_3$ are classical Mott-insulators

with the band-gaps ($\Delta E_{\rm g}$) of 0.2 and 1.2 eV respectively whereas in our GGA calculations they are metals. We have found also that the forces acting on the oxygen atoms in the GGA are quite big (~ 0.5 eV/Å) for the experimental crystal structure.

It is well known that in the systems where the value of kinetic energy is comparable with the value of one site Coulomb interaction and strong electron-electron correlations take place, GGA (or LDA) approximation may fail in the prediction of the correct ground state. The reason is an underestimation of the strong correlations in DFT. In order to take into account the one site Coulomb interaction we use the LDA+U approach which has orbitally lm-dependent potential and describes well the insulating compounds with the long range magnetic ordering. In the LDA+U approach the potential is defined [23, 24] as

$$V_{\sigma jl}^{\rm LSDA+U} = V^{\rm LSDA} + (U-J)[\frac{1}{2}\delta_{jl} - \rho_{jl}^{\sigma}], \tag{1}$$

where ρ_{jl}^{σ} is the density matrix of d electrons.

The value of the Coulomb parameter $U_{3d}^{\rm Ti}$ was varied from 1 up to 5 eV. Since the value of the intra-atomic Hunds rule exchange parameter is almost independent on materials [23] we use a fixed value $J = 1$ eV. The results of the GGA+U calculations for $LaTiO_3$ and $YTiO_3$ with $U_{3d}^{\rm Ti}$=3 eV are shown by black color in fig. 1. In both cases the oxygen bands are slightly higher in energy ~ 0.1 eV in comparison with the GGA results. The t_{2g} band is splitted and the value of the gap is equal to 0.4 eV and 0.6 eV for $LaTiO_3$ and $YTiO_3$ respectively. The magnetic moment per Ti ion in $LaTiO_3$ grows fast with the value of Coulomb interaction and saturates to $0.83\mu_{\rm B}$ at $U_{3d}^{\rm Ti} \simeq 4$ eV (see fig. 2). The experimental magnitude of the magnetic moment for $LaTiO_3$ corresponds to $U_{3d}^{\rm Ti} \simeq 2$ eV in our calculations. The insulating gap appears at $U_{3d}^{\rm Ti} \simeq 3$ eV. In contrast to the GGA calculation the ground state of $LaTiO_3$ is the G-type AFM with the energy gain relative to other types of magnetic ordering of 68 (FM), 85 (C-type AFM) and 23 meV (A-type AFM). In $YTiO_3$ the value of gap increases with the magnitude of the Coulomb interaction (*not shown*). The experimental gap of 1.2 eV wide corresponds to parameter $U_{3d}^{\rm Ti} = 4$. The magnetic moment in $YTiO_3$ (fig. 2) is almost constant and equal to ~ 0.8 eV. The ferromagnetic solution is the lowest in energy.

In fig. 2 we plot the modules of the forces acting on O1 and O2 atoms versus the value of the Coulomb interaction. One can see the forces for O1 and O2 in $LaTiO_3$ and O2 in $YTiO_3$ reduce with increasing of $U_{3d}^{\rm Ti}$ and reach their minimum at about 3.5 eV. The forces for O1 in $YTiO_3$ increase with $U_{3d}^{\rm Ti}$. This fact can be related to the high temperature structure used, thus we expect large distortions in $YTiO_3$ below $T_{\rm C}$. The value of $U_{3d}^{\rm Ti} = 3-4$ eV is in good agreement with the previous experimental [2, 28] and theoretical [18] estimations.

The directions of the forces calculated in the GGA and GGA+U ($U_{3d}^{\rm Ti} = 3$ eV) approximations are shown in fig. 3 by yellow and blue colors respectively. In the case of the GGA method one can see that in $LaTiO_3$ they are almost equal in absolute value and trend more to rotate the octahedra than to distort them. In $YTiO_3$ the two inward forces face nearly along Ti–O bonds, while the two rest outward ones rotate. Thus the GGA method tries to make the structure more cubic. That is a characteristic of the titanates at temperatures above the orbital ordering (700 K [8]) where the electrons become more delocalized and are better described by the GGA. In the case of GGA+U the forces smoothly decrease and rotate with increasing of $U_{3d}^{\rm Ti}$ (*not shown*). At $U_{3d}^{\rm Ti} = 3$ eV the angle between GGA and GGA+U forces is $\sim 90^o$ in $LaTiO_3$ and $\sim 30^o$ in $YTiO_3$ (fig. 3).

In order to visualize the resulting orbital ordering we plot the charge density in fig. 3 for both titanates integrated in the energy window from -2 eV till Fermi level. In this energy interval the charge density has predominant Ti-t_{2g} character. One can see different types of ordering in $LaTiO_3$ and $YTiO_3$: whereas in $LaTiO_3$ the orbitals arrange in a "fish bone" style

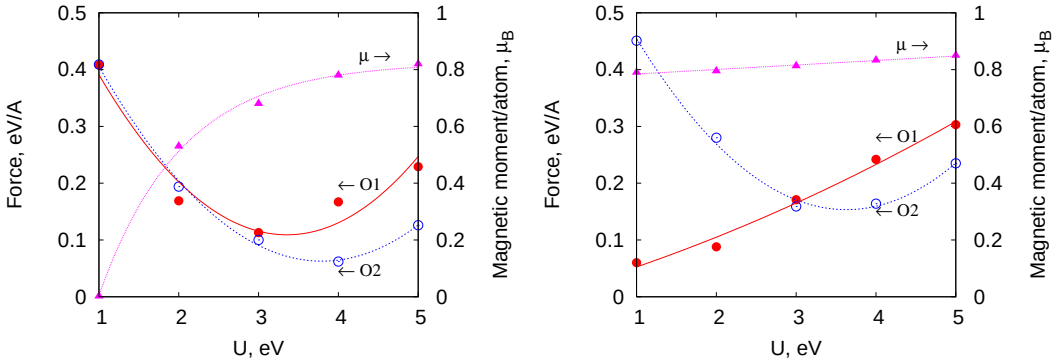

Fig. 2 – (*color online*) The one site electron-electron interaction energy (U) dependency of the modules of the forces acting on different atoms in $LaTiO_3$ (*left*) and $YTiO_3$ (*right*).

they form a rhombus in $YTiO_3$. These results agree with those reported in previous theoretical findings [10] and experimental works [7, 14–16]. The presented electronic densities clarify the mechanism of the lattice distortions. Because of the repulsion between negatively charged orbitals and oxygen atoms the different types of OO cause differnt types of the distortions. The orbitals in $LaTiO_3$ do not face toword any oxigens, thus distortions of the octahedra are small there and their rotations are dominant. On contrary in $YTiO_3$ a specific elongation of the orbitals toword O-atoms makes strong distortions of the octahedra favourable. Since OO in the GGA calculations is weak the corresponding forces face face opposite direction. Thus taking into account the one site electronic correlations with the energy of Coulomb interaction around $3-4$ eV we obtain a correct type of the orbital ordering and can describe the crystal distortions.

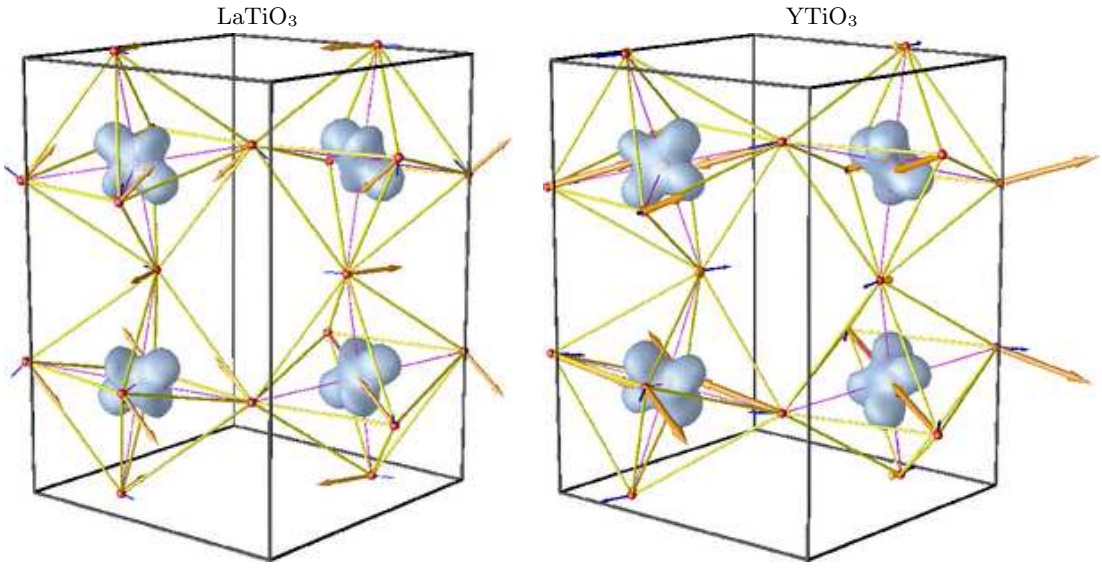

Fig. 3 – (*color online*) Charge densities in the energy window from -2 eV till EF (gray surface). Arrows are forces acting on atoms in GGA (*orange*) and GGA+U with $U_{3d}^{\mathrm{Ti}} = 3$ (*blue*). $U_{4f}^{\mathrm{La}} = 8$ eV.

Conclusions. – We have found the correct magnetic and electronic ground state for $LaTiO_3$ and $YTiO_3$ in the framework of the GGA+U calculations. The value of Coulomb interaction parameter estimated from the minimum of the forces is about $3-4$ eV. This is in good agreement with the previous theoretical studies and photoemission experiments [11]. In $YTiO_3$ in the GGA+U method with the optimal U-values the band-gap is $0.6-1.2$ eV and the magnetic moment is $\mu = 0.81 - 0.83\mu_{\rm B}$ in a good agreement with experimental data. The values of $\mu = 0.7\mu_{\rm B}$ and gap $E_{\rm g} = 0.4$ eV for $U_{3d}^{\rm Ti} = 3$ eV in $LaTiO_3$ are overestimated because of the absence of the magnetic fluctuations in GGA+U [10]. The orbital order found for all values of $U_{3d}^{\rm Ti}$ is "fish-bone" and rhombus-type for $LaTiO_3$ and $YTiO_3$ respectively and is consistent with experimental structure findings.

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